Drinking Water Quality Deterioration in Distribution Systems: Colored Water Formation and Its Control

Vernon L. Snoeyink
Ivan Racheff Professor of Environmental Engineering
Department of Civil and Environmental Engineering,
University of Illinois at
Urbana-Champaign

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Outline

- Background
- Conceptual model of tubercles
- Iron release: mechanism and control
- Particle formation
- Conclusions

Effects of Iron Scales and Iron Release

- Particle formation
- Discolored water
- Staining of fixtures, clothing
- Metallic tasting water
- Flow restriction
- Oxidant demand
- Biofilm

Corrosion is different from Iron Release

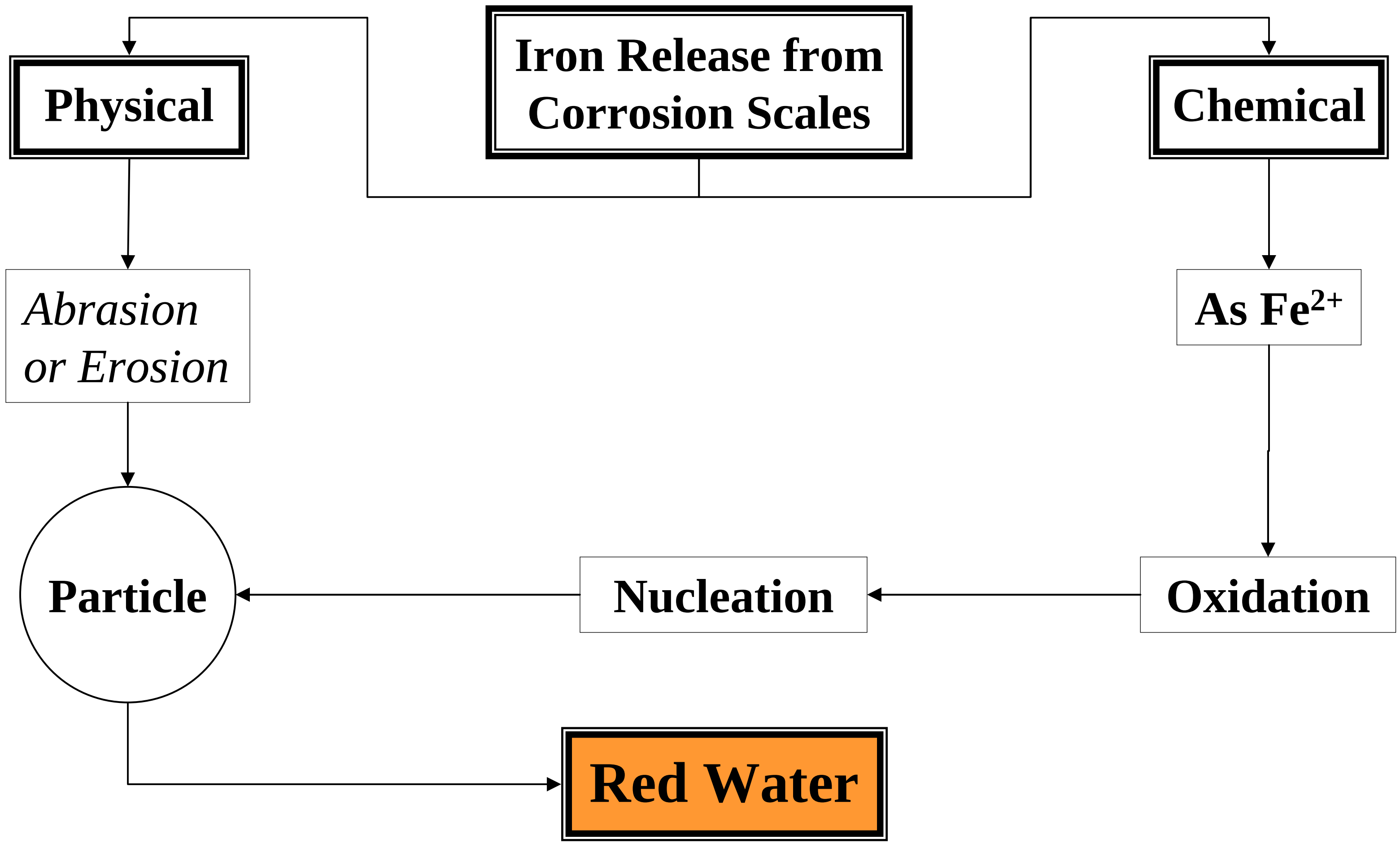
Corrosion *of iron is the conversion of "metallic iron" to an oxidized form, either soluble or an oxidized scale.*

- $Fe \rightarrow Fe^{2+} + 2e^{-}$
- Usually measured as weight loss from metallic iron

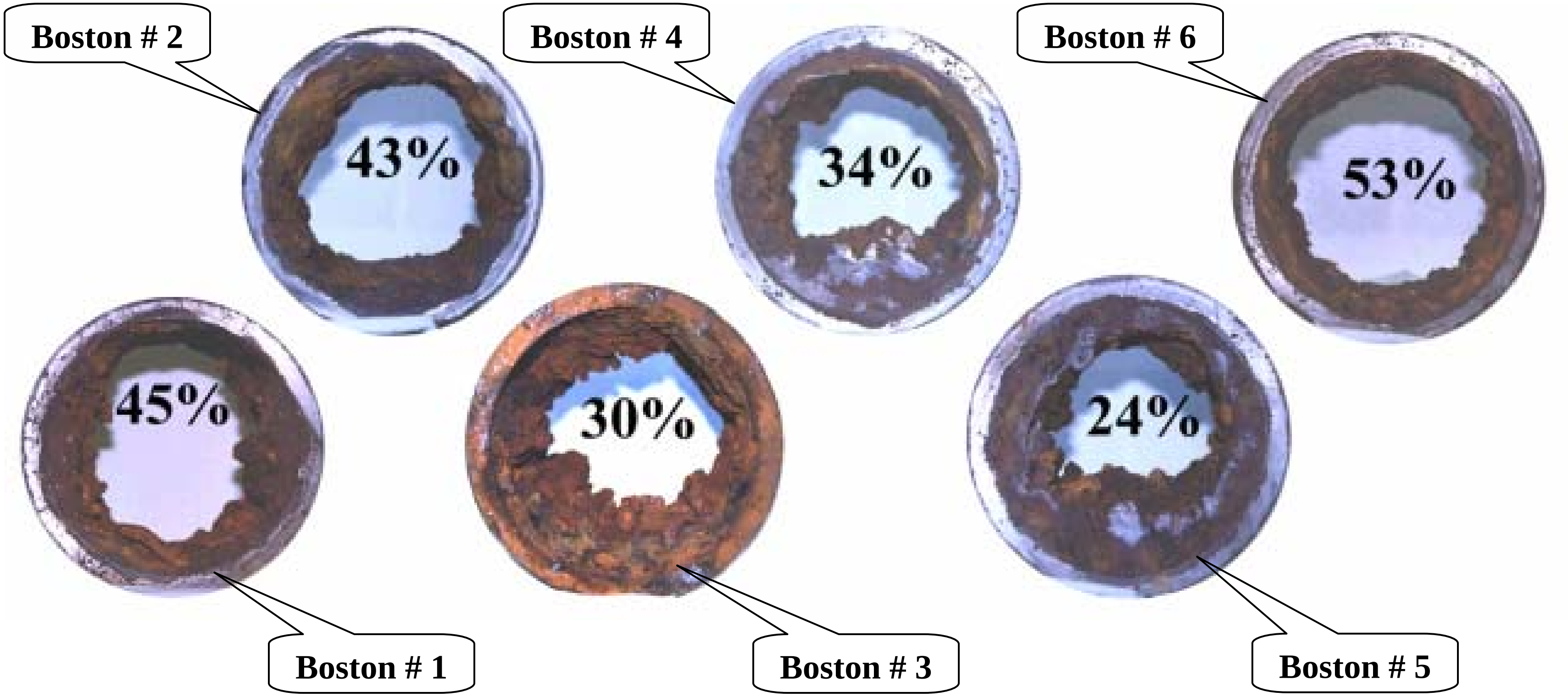
Iron release *is the transport of iron, in soluble form or as a particle, from corrosion scale or metal to bulk water.*

- Cumulative effect of *corrosion, hydraulic scouring and dissolution of corrosion scales.*
- Usually measured as concentration of iron in bulk water

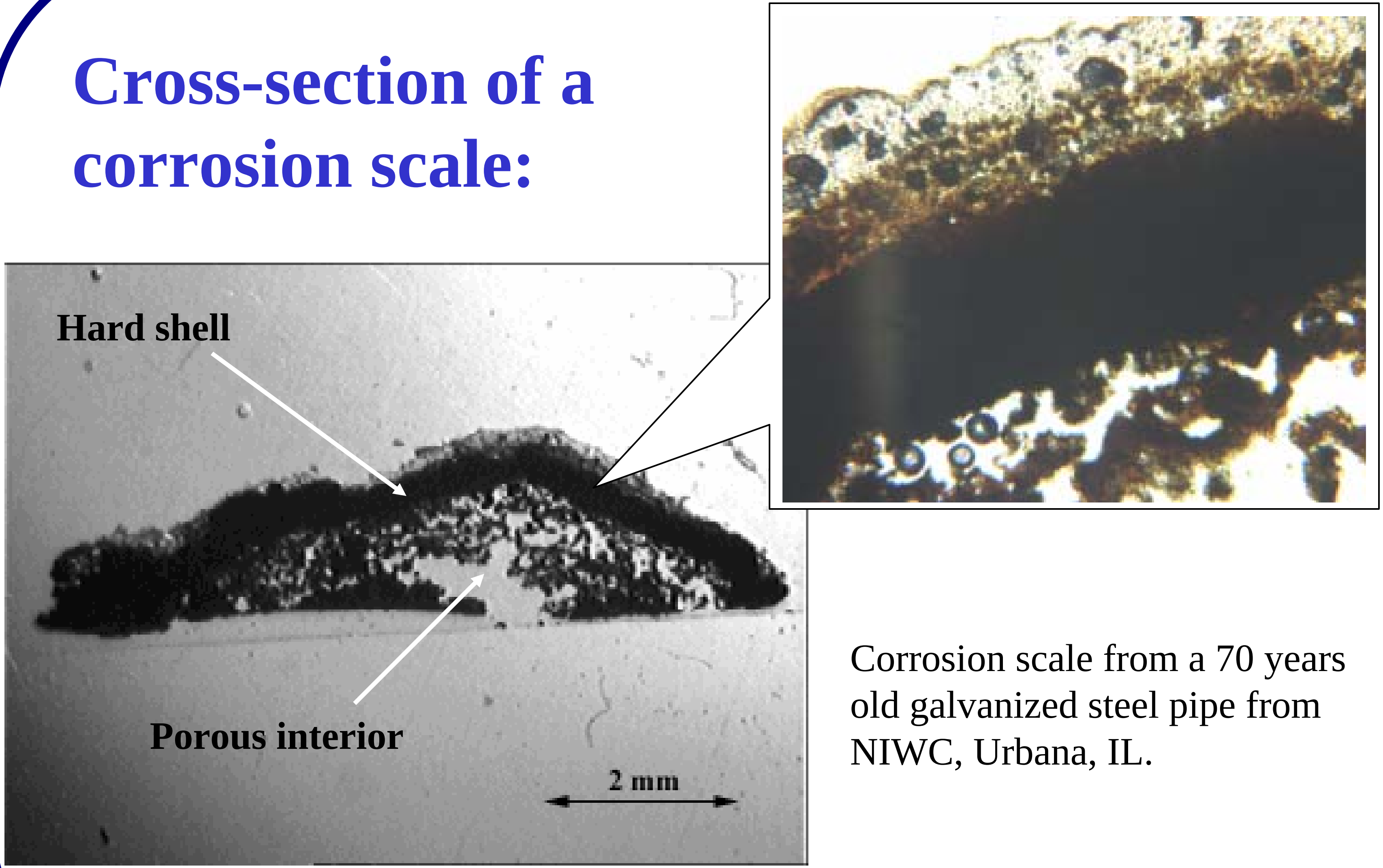
“Red Water” Formation



Available cross-section for flow – MWRA Cast Iron Pipes

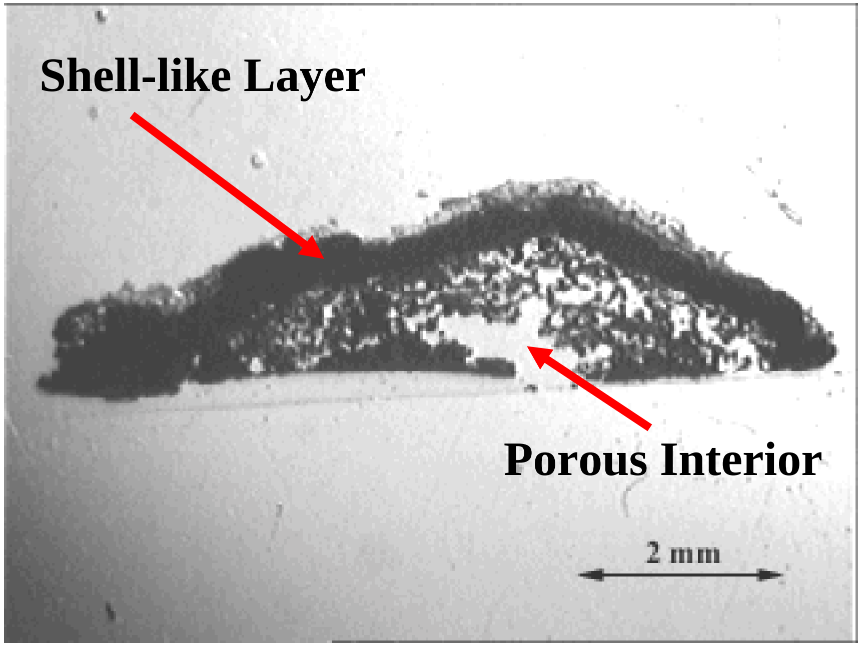


Cross-section of a corrosion scale:



Corrosion scale from a 70 years old galvanized steel pipe from NIWC, Urbana, IL.

Scale Structure and Composition



- Corrosion scales are ***porous deposits*** with a hard ***shell-like layer***
- ***Reservoir of Fe(II)*** ions exists in the scale interior
- **Composition**
    - ***Shell-like layer:*** Magnetite (Fe_3O_4) and goethite (α-FeOOH)
    - ***Porous Interior:*** Mostly Fe(II) compounds, green rusts (possible), and ???
    - Fe(III) compounds present only in the top layers. Also other solids.

Corrosion scales have a "*Reservoir of Fe^{2+} ions*"

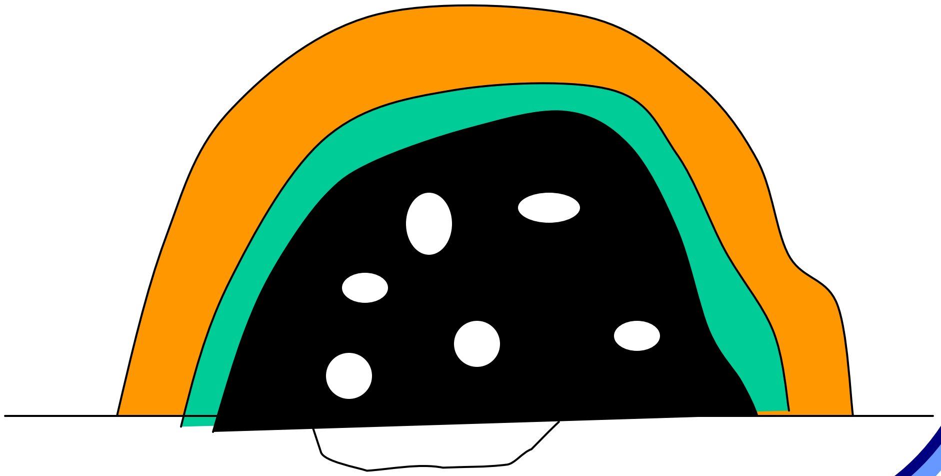
Sample Wet Chemistry Analysis

Sample Details		% Ferrous	% Ferric
Sample I.D.	**Sampling Position**		
NIWC-A	Entire Scale	31	69
Boston # 3	Top	4	96
	Middle	94	6
	Bottom	92	8
Boston # 6	Top	28	72
	Middle	80	20
	Bottom	80	20

Tubercle Structure

1. Corroded floor
2. Internal cavity solid
3. Internal cavity fluid
4. Shell-like layer
5. External crust

After H. Herro, Nalco Chemical

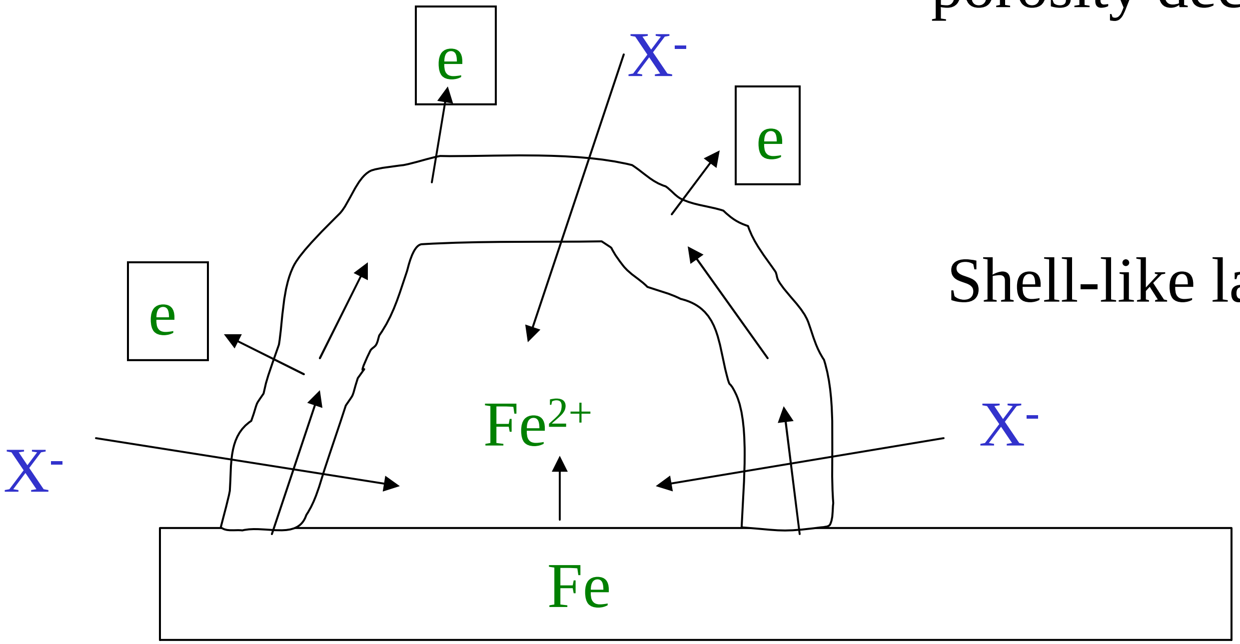


Electron/Charge Flow in a Tubercle
Alternative 2, DO Present

$Fe^{2+} + 2\ H_2O \rightarrow Fe(OH)_{2(s)} + 2\ H^+$

$4\ e + O_2 + 4\ H^+ \rightarrow 2\ H_2O$

$CaCO_3$ may form if pH increases. Will porosity decrease?



Shell-like layer

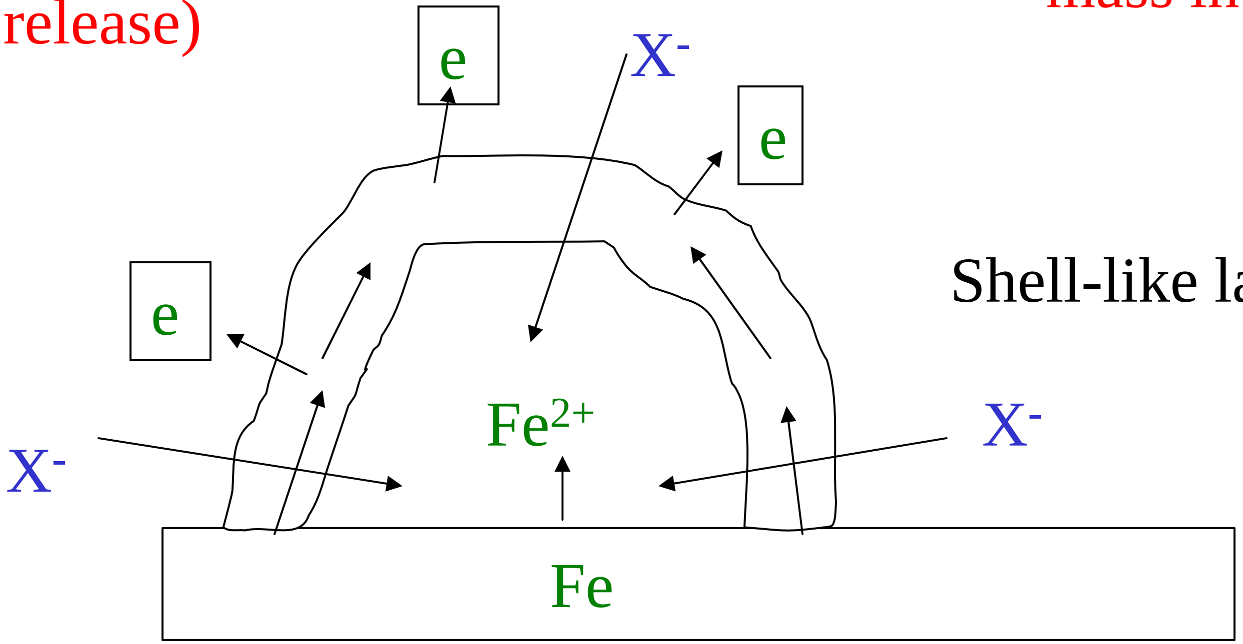
Electron/Charge Flow in a Tubercle
Alternative 3, DO Absent (Kuch Mechanism)

$Fe^{2+} + 2\ H_2O \rightarrow Fe(OH)_{2(s)} + 2\ H^+$

$e + FeOOH + 3\ H^+ \rightarrow Fe^{2+} + 2\ H_2O$

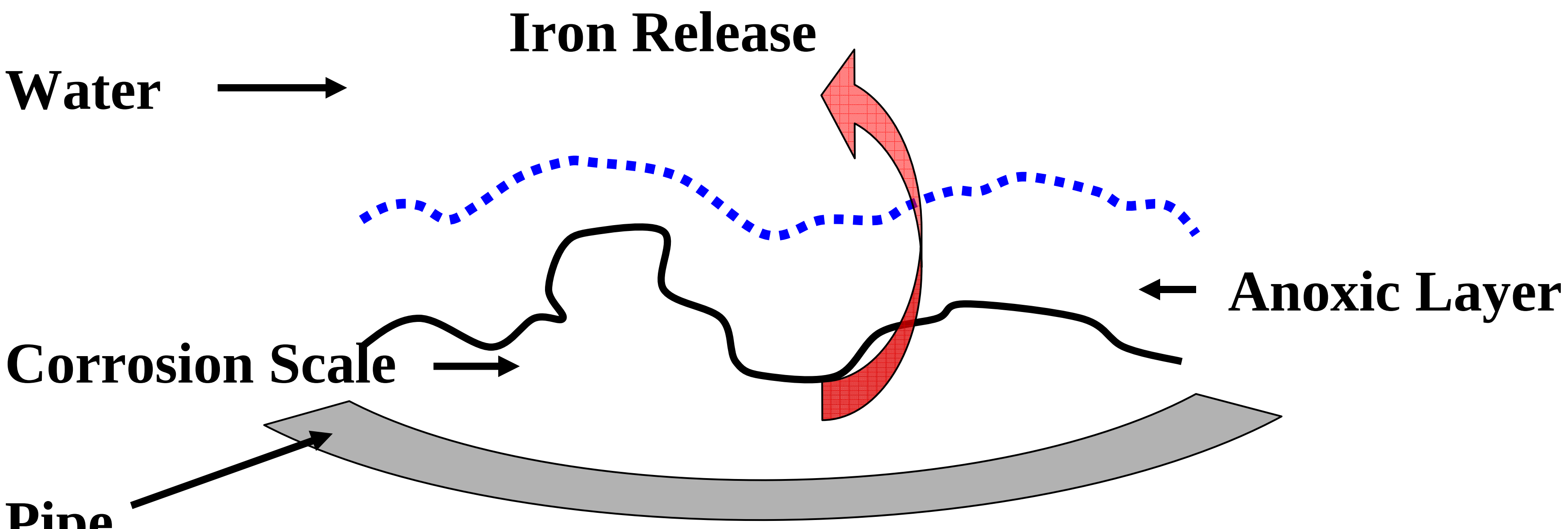
(iron release)

Tubercle growth from mass increase



Shell-like layer

Mechanism of Iron Release



Iron Release Mechanisms (Possible)

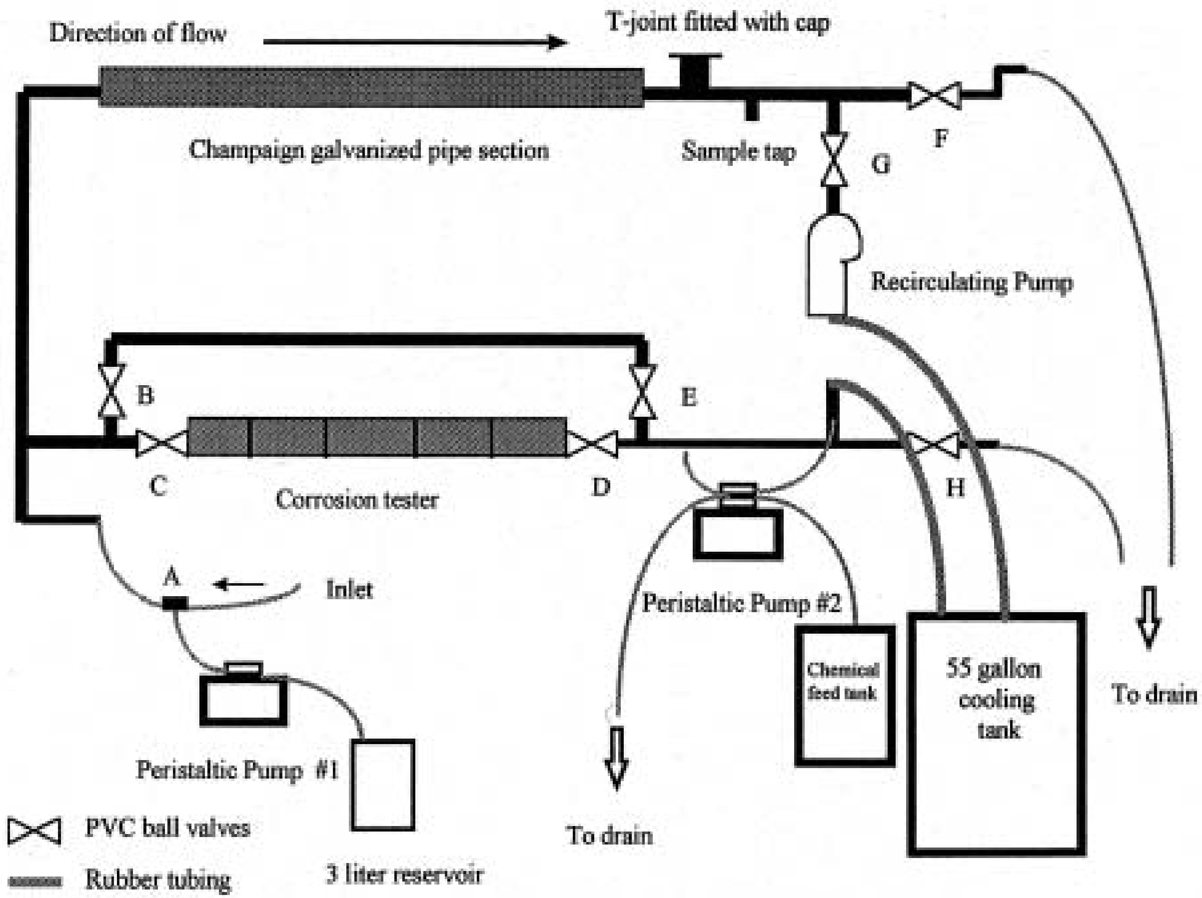
1. Kuch Mechanism

2. *Porous* shell-like layer: Fe^{2+} diffuses into bulk solution

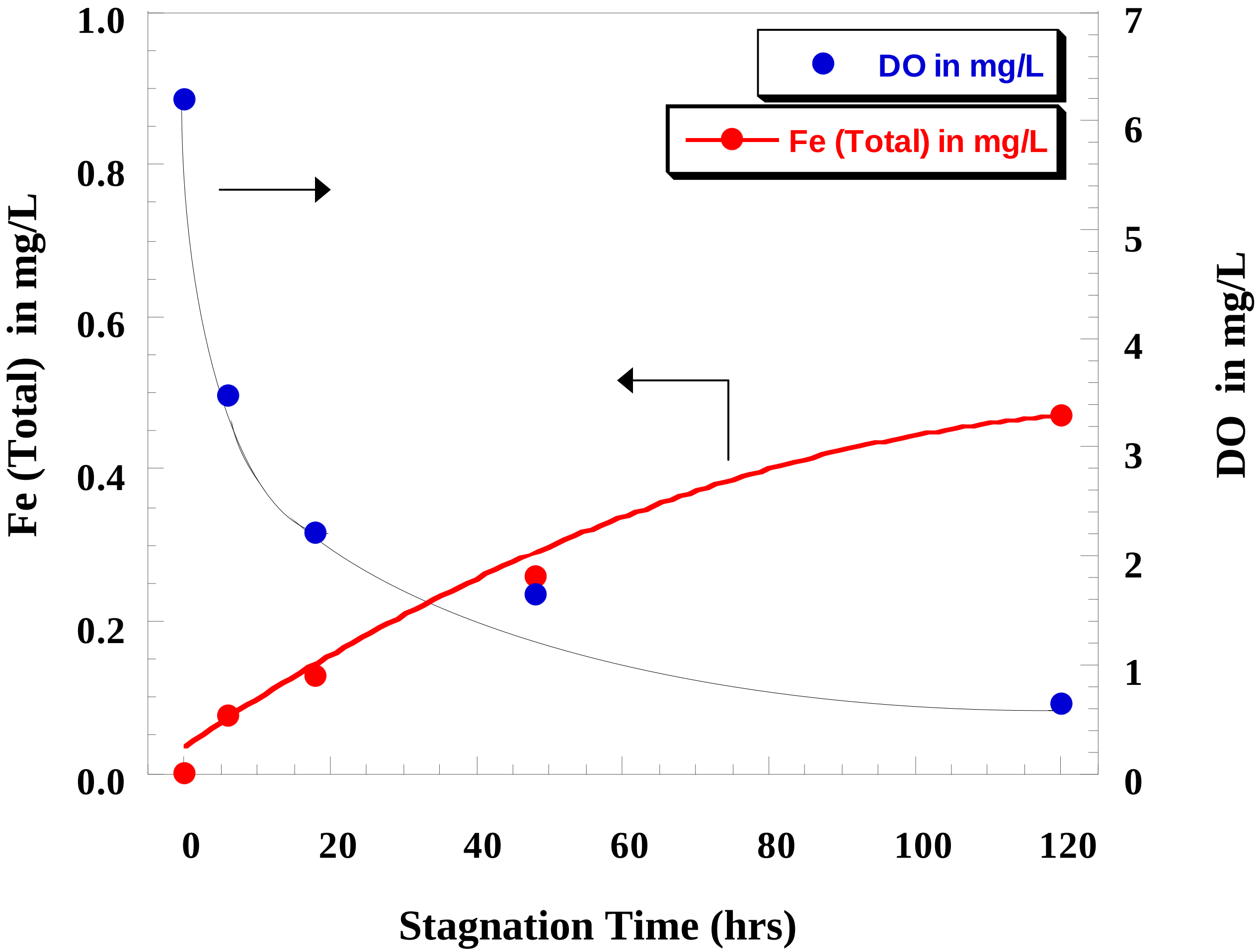
3. *Fracture* of the shell-like layer: Fe^{2+} solution is released from the tubercle cavity

Other: Reduction by organic matter; microbial processes. Not discussed here.

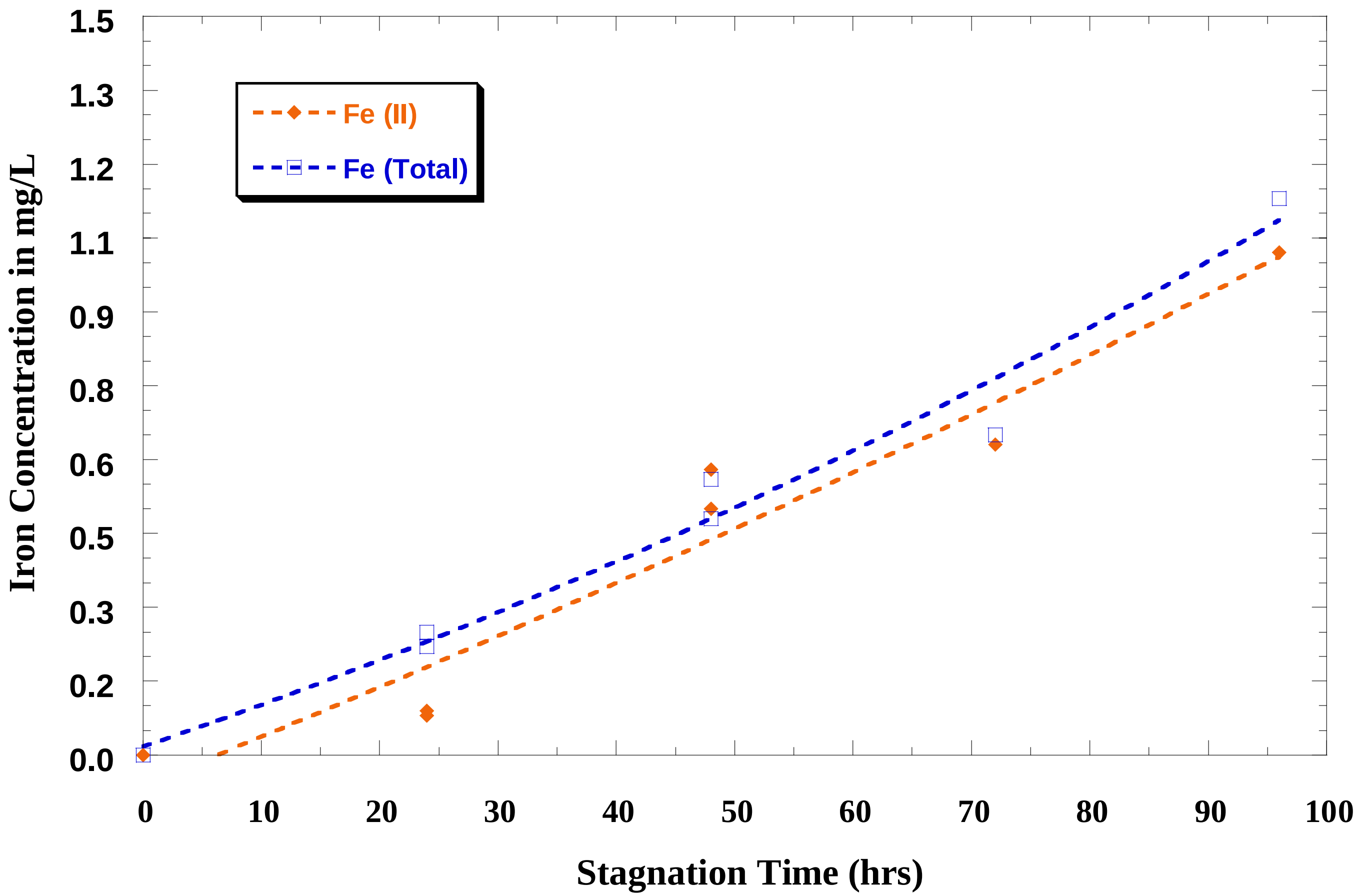
Pipe Loop Setup



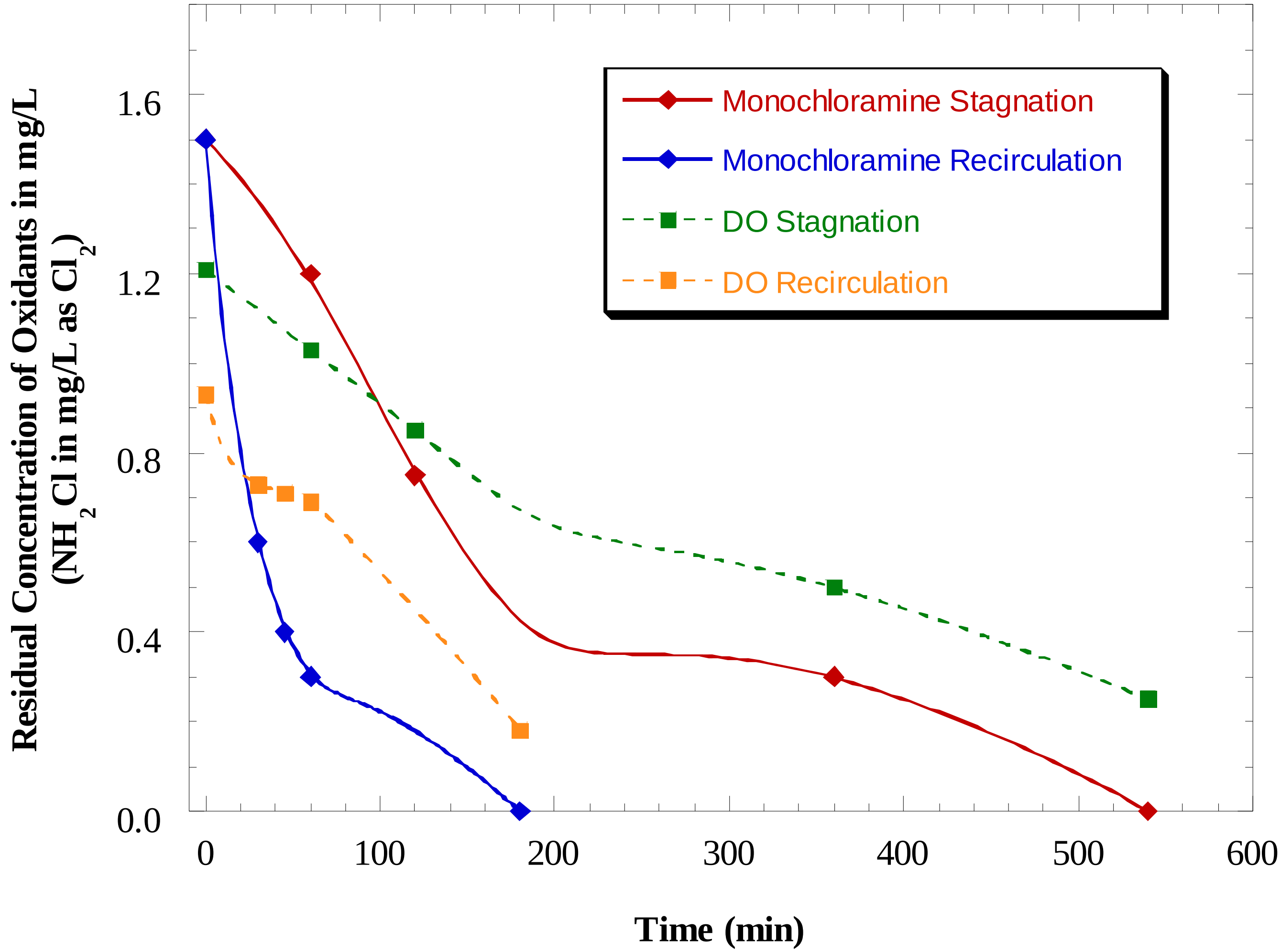
Iron Release – Effect of DO (NIWC Pipes)



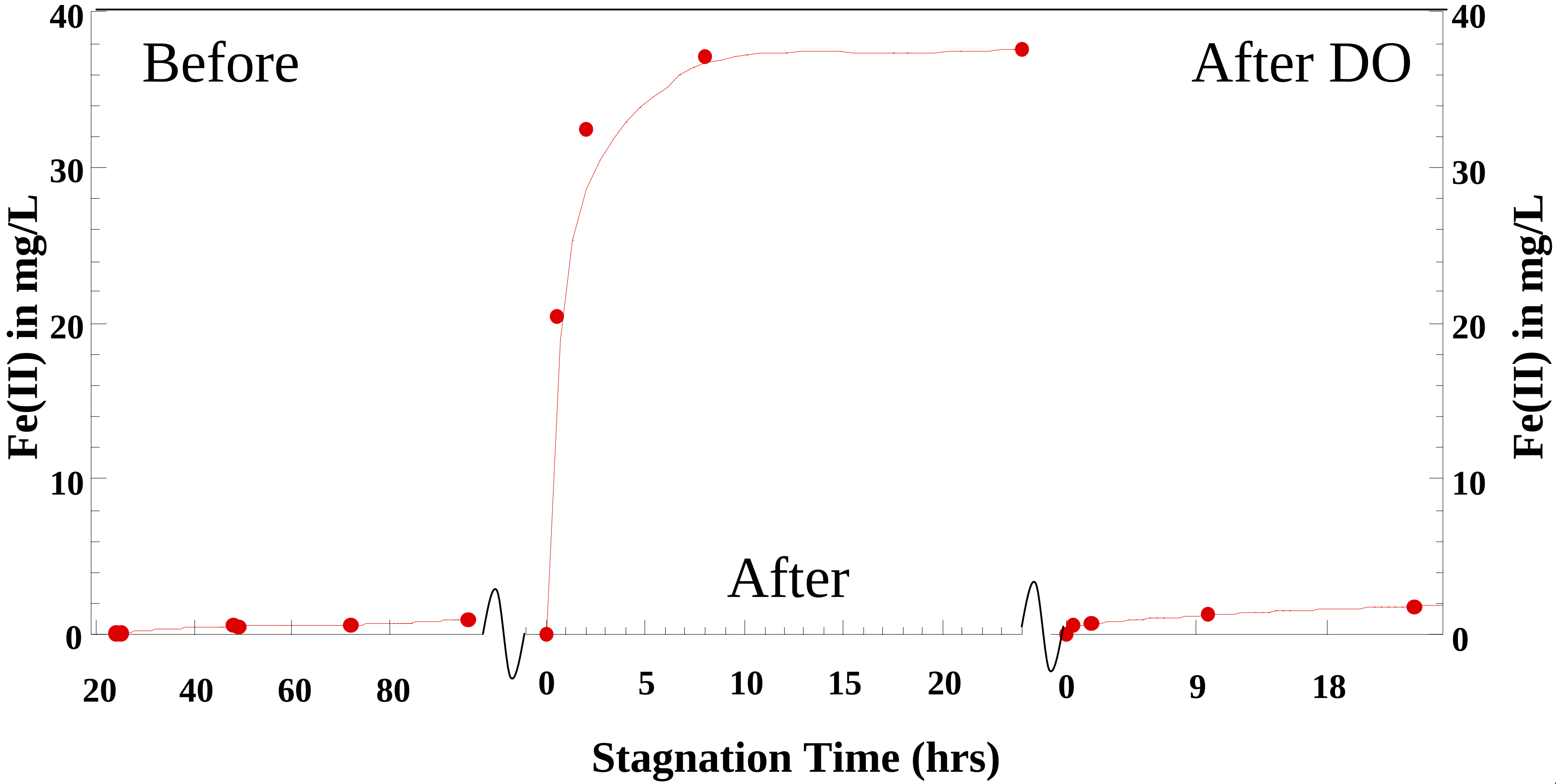
Iron is Released from Corrosion Scales as “ Fe^{2+} ”



Chlorine and Oxygen Residual - Flow and Stagnation (NIWC Pipes)

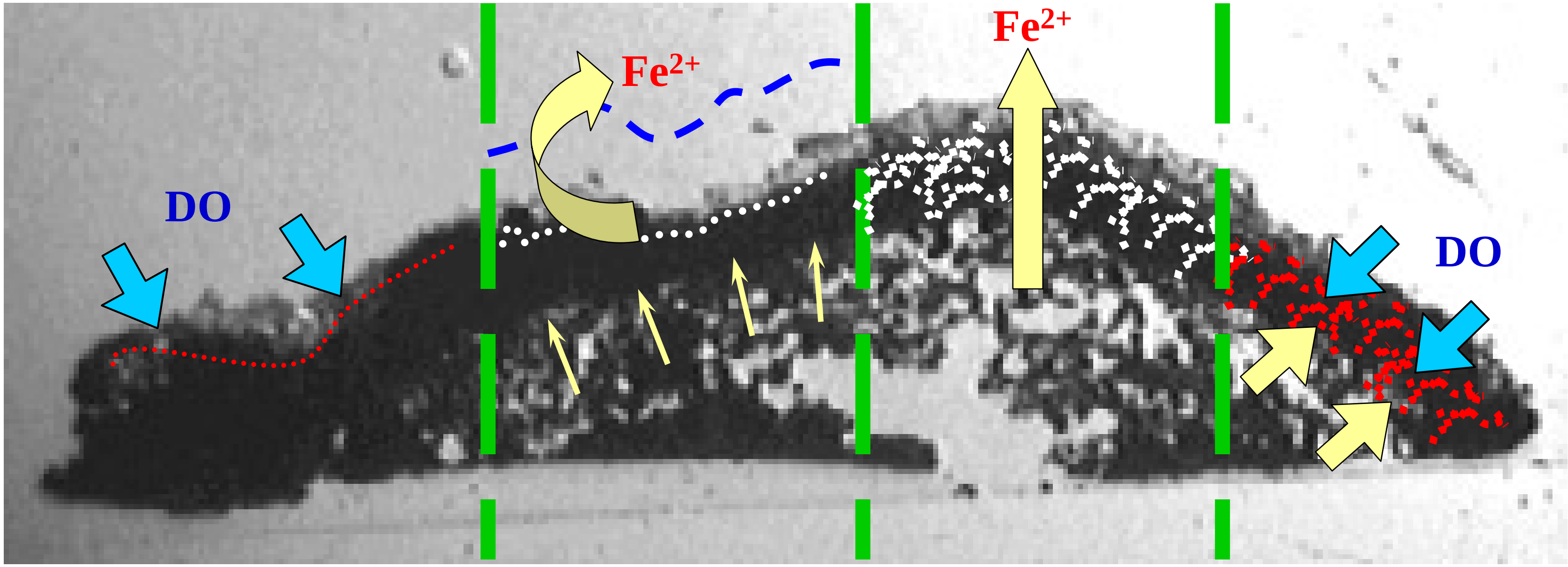


Iron Release – Extended Exposure to Anaerobic Conditions (NIWC Pipes)



Iron Release from Corrosion Scales

Flowing Water with oxidants	Stagnant Water with oxidants "Anoxic layer"	Prolonged Stagnation	Oxidant supply restored



Conclusions and Implications of the Conceptual Model

- Fe II dissolution = iron release = colored water
- Stagnation promotes Fe II dissolution
- Stagnation increases shell-like layer porosity
- So, avoid stagnation
- Iron release is reduced by scale oxidation
- So, keep oxidants next to pipe wall
- Avoid changes in pH and alkalinity
- Avoid increases in TDS
- Keep pH near pH_s for $CaCO_3$ precipitation

Key Iron Release Model Features

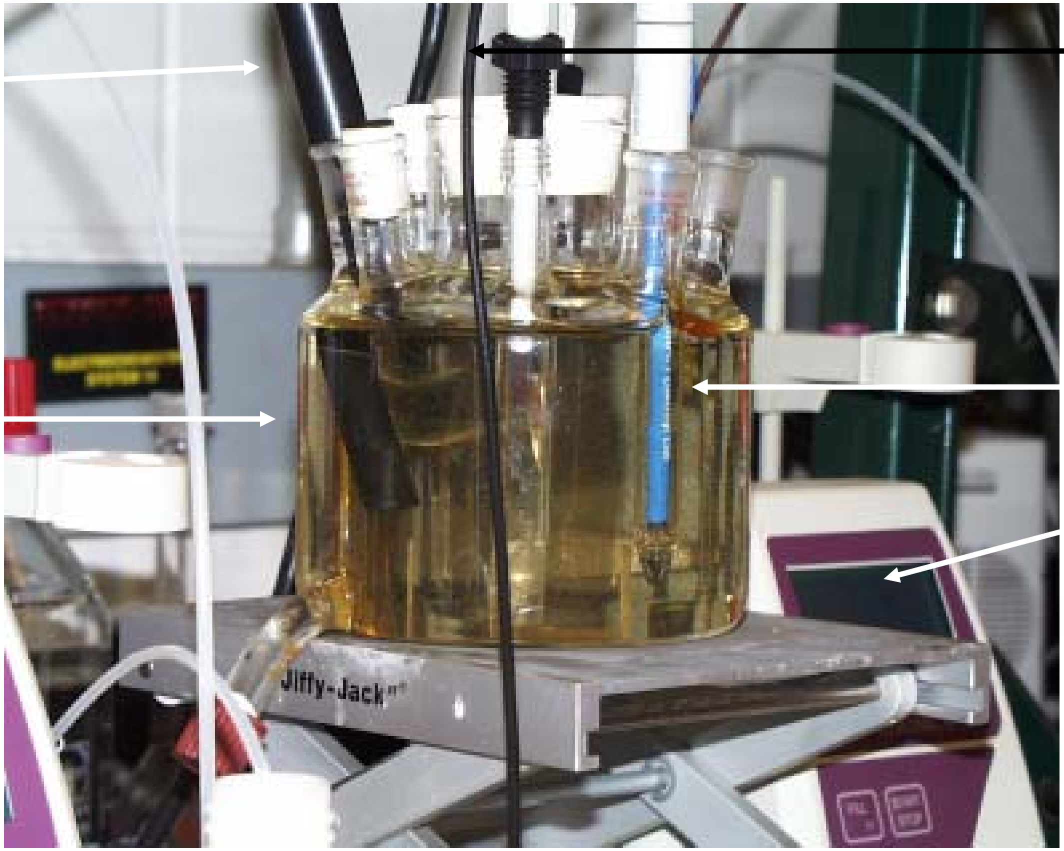
Role of Particles/Colloids

- When oxygen and chlorine are in contact with scale, ferrous ions are oxidized within the scale or close to the surface- *the iron is incorporated into the scale*
- When oxidants are not present at the surface, ferrous iron can diffuse into solution and is oxidized there- *particles form in the water*

Particle Generation Reactor

DO electrode

Gas feed line



1.2 L cell

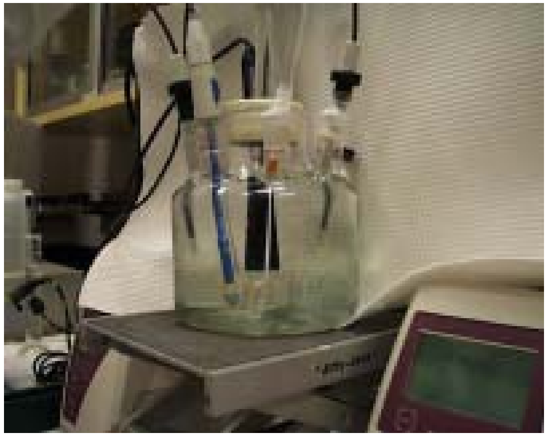
pH electrode

Acid/base titrator

Color Development in High pH (10) and High DIC (100 mg C/L) Water

5 mg Fe/L, 23° C, PO_2=0.122 atm

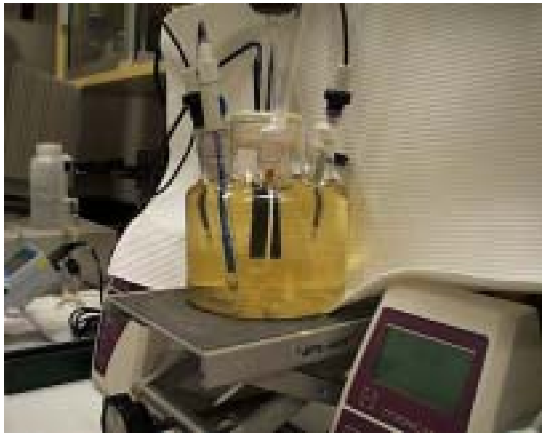
5 seconds



15 seconds

45 seconds

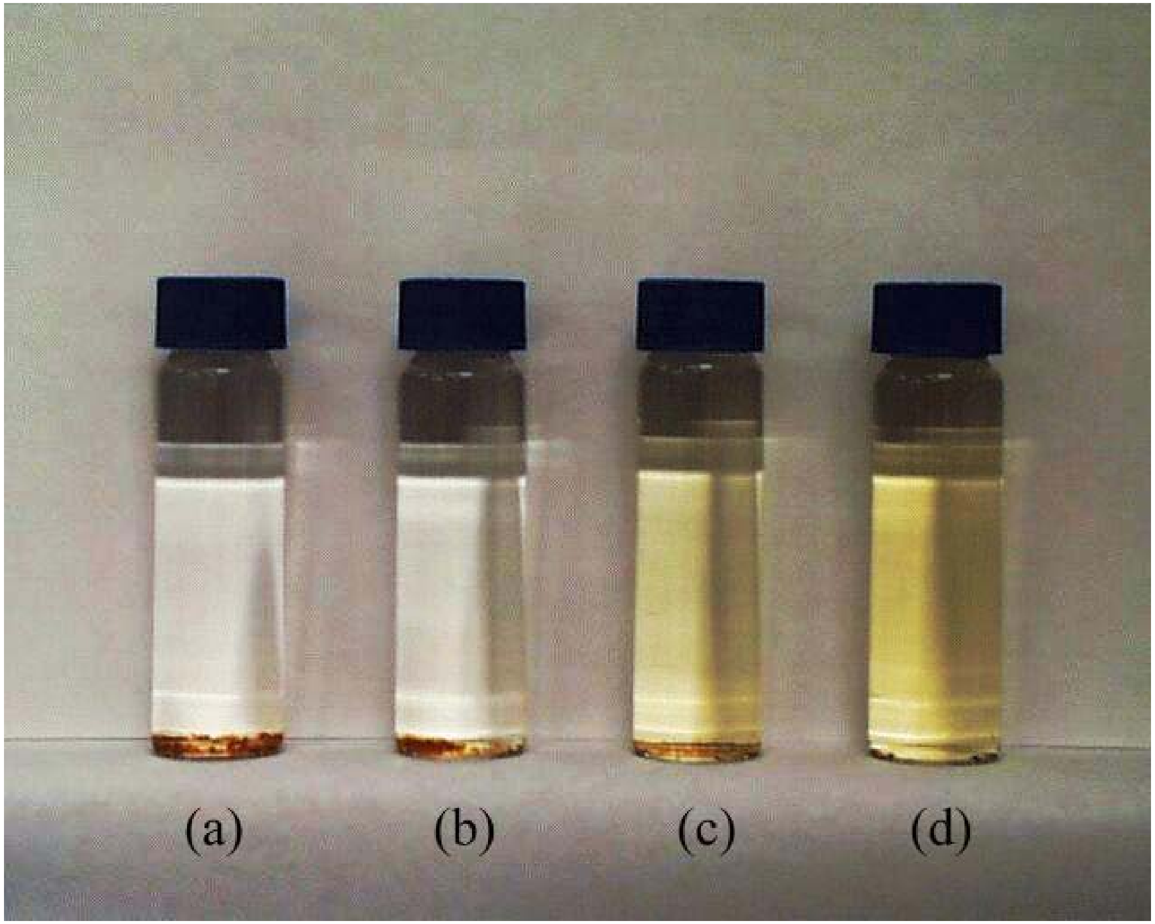
180 seconds



The Effect of pH on the Stability of Iron Suspensions

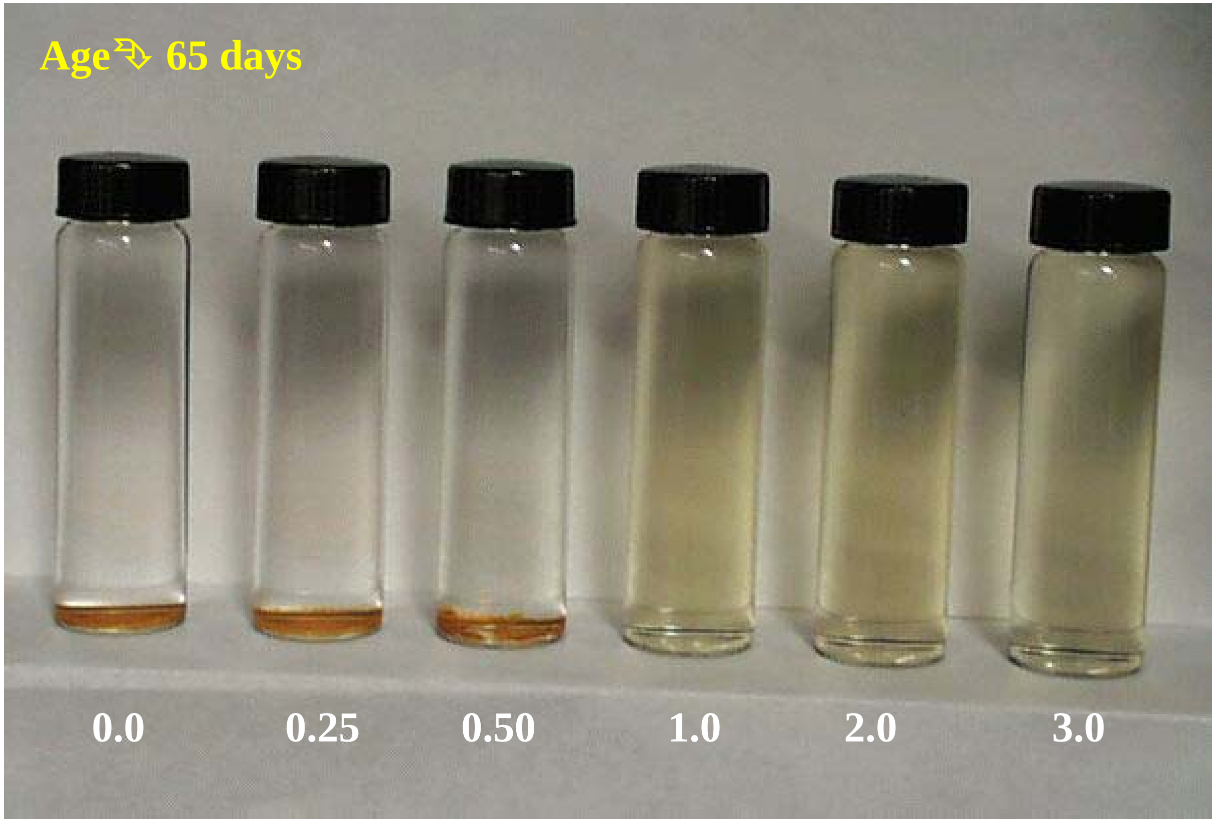
5 mg Fe/L, DIC= 5 mg C/L, 22° C, PO_2=0.122 atm

pH= (a) 6, (b) 7, (c) 8, and (d) 9



Effect of Orthophosphate on Iron Suspension Stability

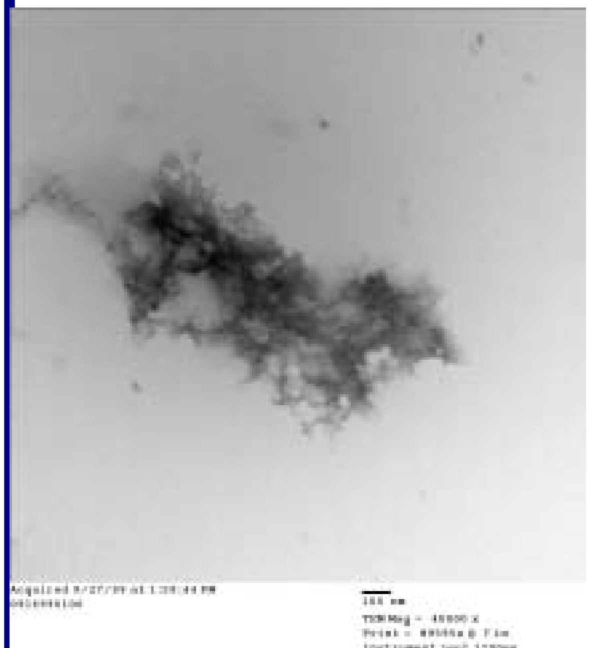
5 mg Fe/l, PO_2= 0.122 atm, pH=8, DIC= 5 mg C/L, 22 ^{O}C



The Effect of Orthophosphate on Iron Colloids

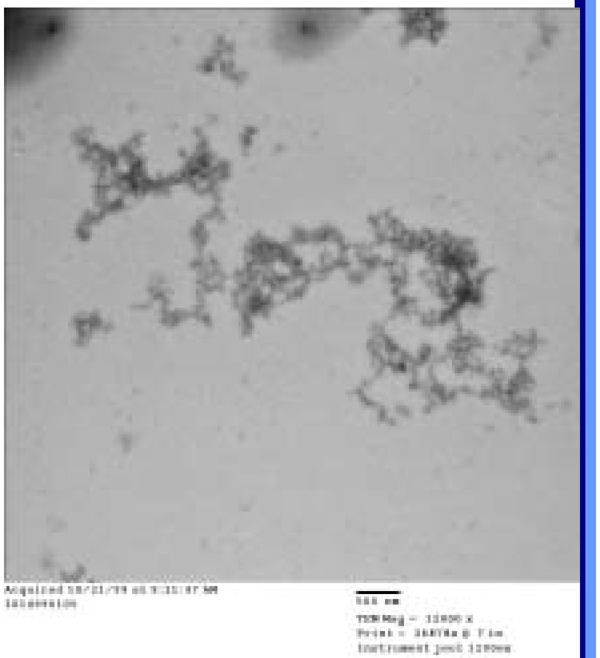
TEM micrograph of iron particles

1 mg Fe/L, pH=7.85 to 7.89, 22.5 to 23°C, DIC= 5 mg C/L, PO_2=0.122 atm



0 mg PO_4/L (crystal)

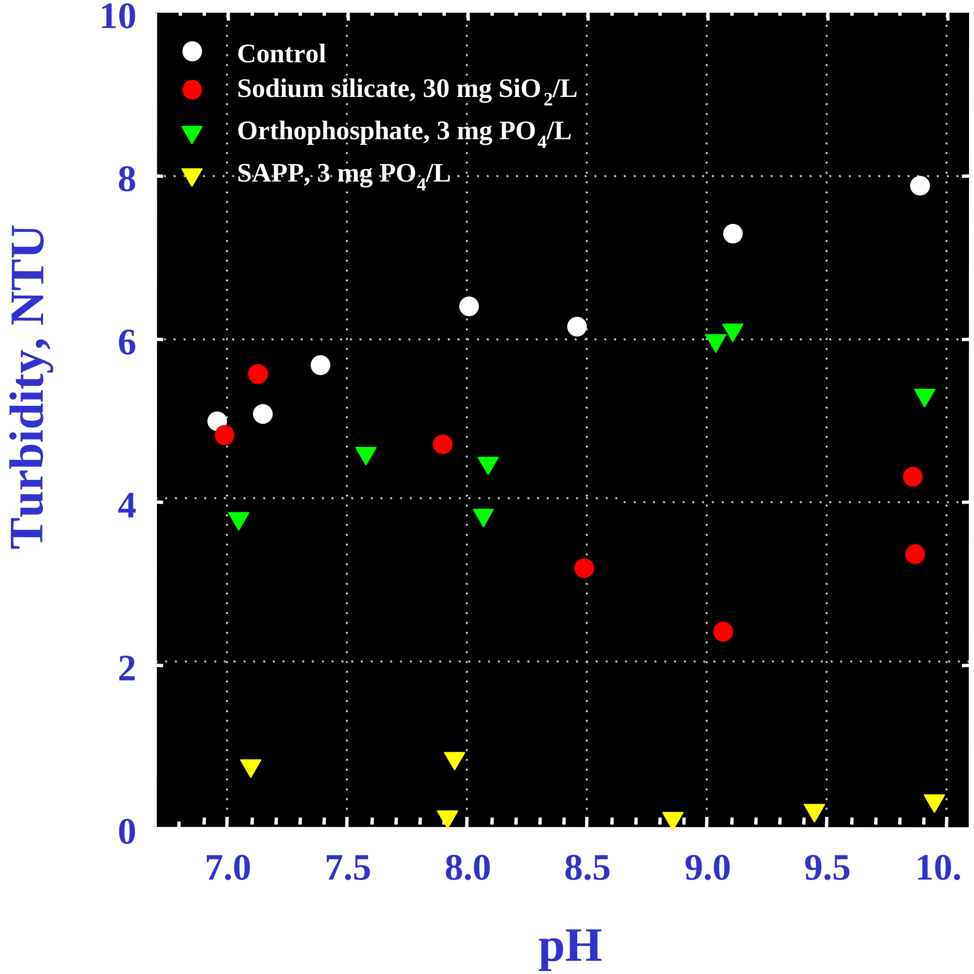
0.5 mg PO_4/L



3 mg PO_4/L (am)

The Effect of "Corrosion Inhibitors" on Turbidity

Fe_{tot}= 5 mg/L, DIC= 5 mg C/L, 0.122 atm O_2,, 23°C



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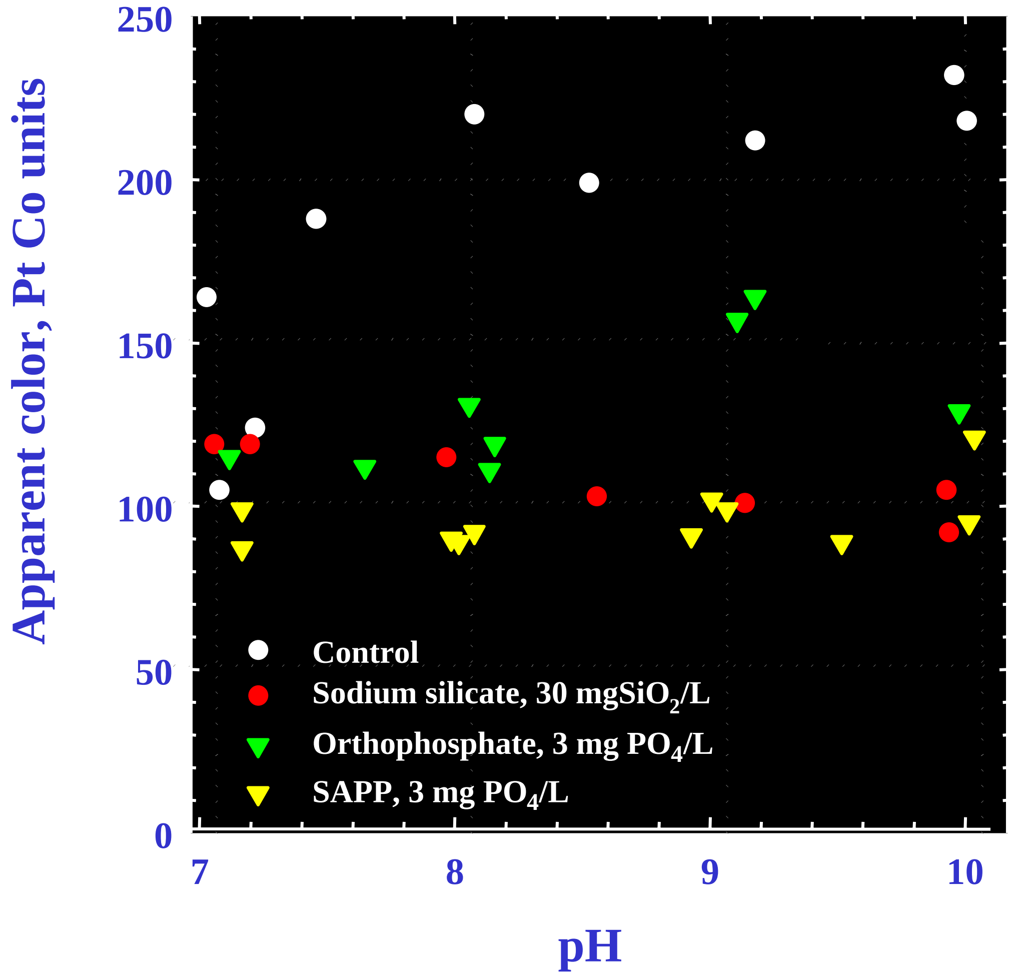
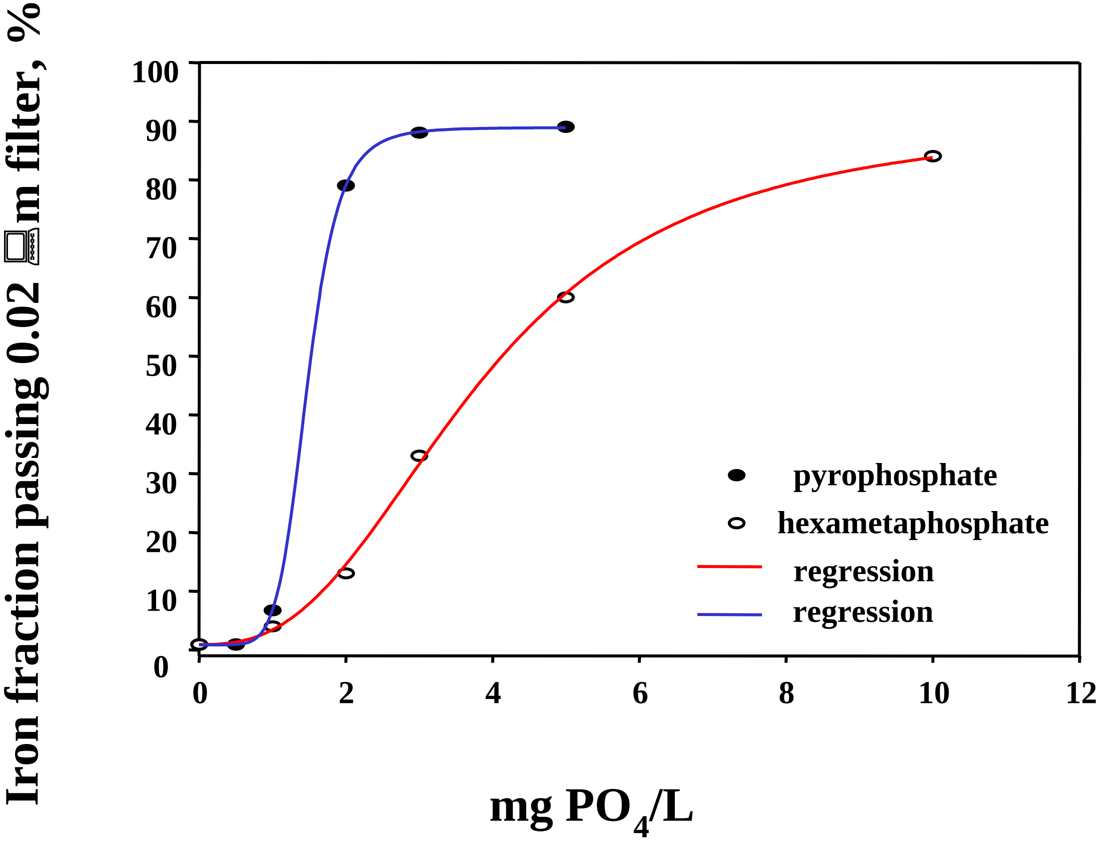
The Effect of Corrosion Inhibitors on Color

Fe_{tot}= 5 mg/L, DIC= 5 mg C/L, 0.122 atm O_2,, 23°C



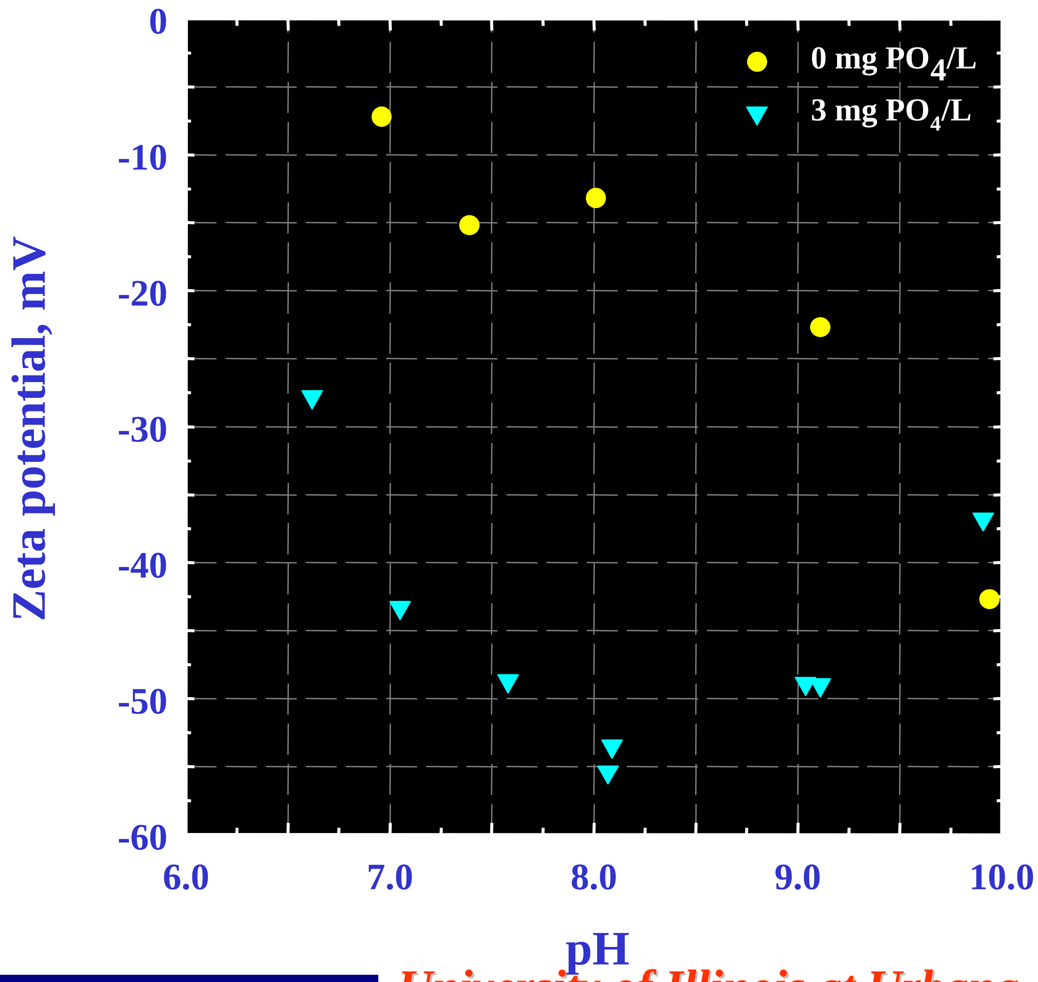
The Effect of Polyphosphate on Filterable Iron

DIC=5 mg C/L, pH=8, Fe II = 1 mg/L



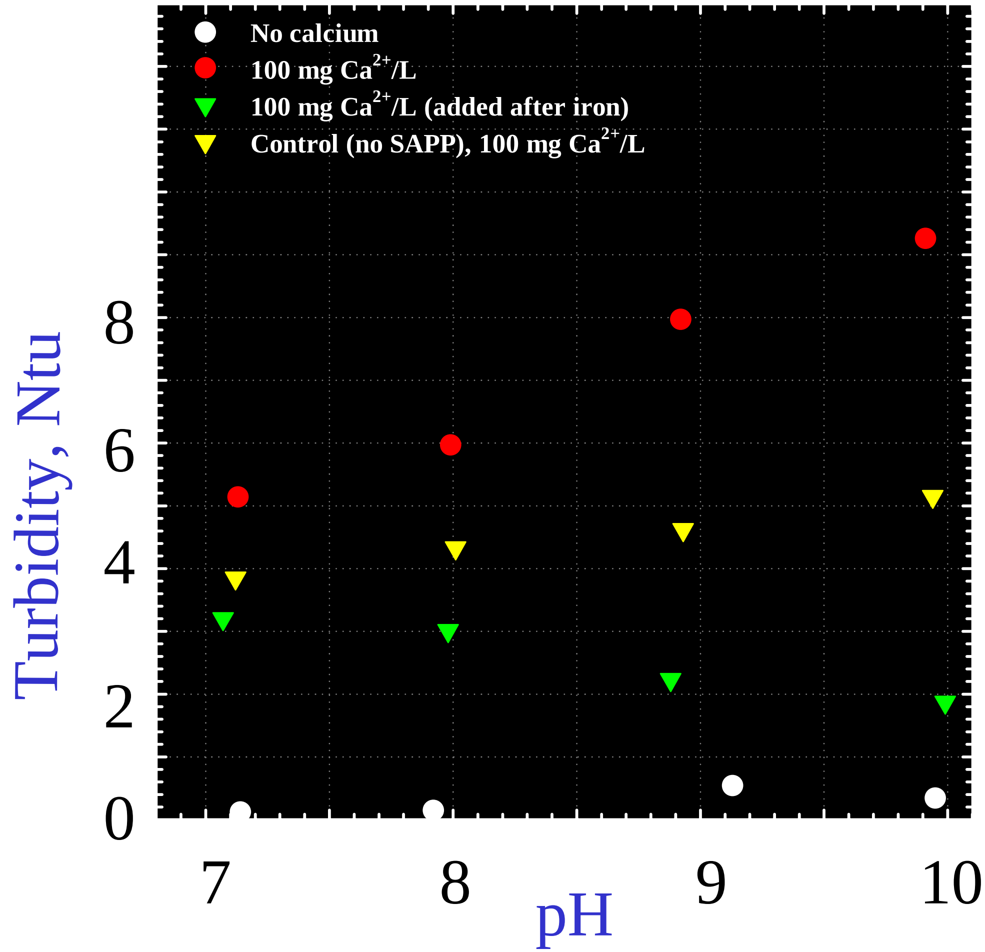
The Effect of Orthophosphate and pH on ZP

Fe_{tot}= 5 mg/L, DIC= 5 mg C/L, 0.122 atm O_2, 22°C



The Effect of SAPP on Turbidity when 100 mg/L Calcium is Present

Fe_{tot}= 5 mg/L, DIC= 5 mg C/L, 0.122 atm O_2, 22°C, 3 mg PO_4/L



Iron Particles and Iron Suspensions Conclusions

1. Color and turbidity increased with DIC below pH 8 to 8.5
2. Color and turbidity increased linearly with increasing iron
3. Intermediate, short-lived solid formed in higher pH and DIC waters
4. Particle charge and suspension stability increased with increasing pH

The Effect of Phosphates on Iron Particles Conclusions

Phosphates

1. Reduced suspension color and turbidity
2. Became part of the iron colloid
3. Increased the negative charge of iron colloids
4. Stabilized iron colloids
5. Inhibited colloid growth and flocculation
6. But, what is the effect on the scales?

Historical Overview – Importance of Corrosion Scales

Corrosion & Corrosion protection

- ***1920's – 1960's***
  - $CaCO_3$ and rust are components of "good" corrosion scales (Tillmans, Baylis, Larson)
  - Concept of **Langelier Index**
  - Importance of **"Buffer Intensity"** as the most important factor for corrosion control (Stumm)
- ***1975 - 1981*** **Sontheimer, Kölle et al.**
  - Importance of scale structure and composition
  - **"Siderite model for formation of protective scales"**

Iron Release *vs* Corrosion Rate

- ***1984 - 1989*** **Kuch, Sontheimer et al.**
  - Iron Uptake was differentiated from Corrosion Rate
  - First to highlight chemical reduction of corrosion scales as a possible mechanism for *non-steady state corrosion*
  - Concept of easily reducible phase – γ-FeOOH

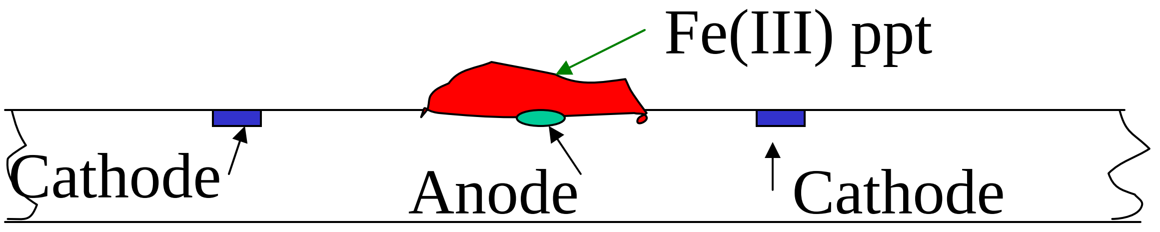
Formation of a Tubercle

At A: $Fe \rightarrow Fe^{2+} + 2\,e$

At C: $\frac{1}{2}\,O_2 + 2\,H^+ + 2\,e \rightarrow H_2O$

At A: $Fe^{2+} + 5/2\,H_2O + \frac{1}{4}\,O_2 \rightarrow Fe(OH)_{3(s)} + 2\,H^+$

N. B.: Must balance charge at A and C



Electron/Charge Flow in a Tubercle
Alternative 1

$Fe^{2+} + 2\ H_2O \rightarrow Fe(OH)_{2(s)} + 2\ H^+$

$2\ H^+ + 2\ e \rightarrow H_2$

Tubercle growth from solid and gas